CATALYTIC HYDRODENITROGENATION OF QUINOLINE WITH NANOSCALE Mo_2N, Mo_2C and MoS_2 SYNTHESIZED BY LASER PYROLYSIS

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INTRODUCTION

As the quality of available petroleum feedststocks decreases, the demand for better and more active catalysts for hydrotreatment increases. Nitrogen content in coal, tar sands, shale and petroleum residua is present predominantly in the form of heterocyclic compounds. Quinoline constitutes a molecule representative of these heterocyclic compounds and its catalytic denitrogenation is one of the most studied model compound reactions. Due to the considerable number of stable reaction intermediates with different absorptivities and reactivities, this reaction is a typical example of the complexity of the denitrogenation process.

Nitrogen removal from heterocyclic compounds is a more difficult process than sulfur removal. It has been accepted that it requires hydrogenation of the ring containing the nitrogen atom before hydrogenolysis of the carbon-nitrogen bond occurs [1,2]. This is partly due to the thermodynamics of the aliphatic C-N bond hydrogenolysis reaction.

Figure 1 shows a diagram of the reaction pathway reported by Satterfield et al [3,4] for the denitrogenation of quinoline over a sulfided $NiMo/Al_2O_3$ catalyst . It is seen that the HDN reaction proceeds through the hydrogenation of quinoline (Q) to 1,2,3,4 tetrahydroquinoline (THQ) and 5,6,7,8 tetrahydroquinoline (CHPYD), the first reaction being faster than the second. THQ can either convert into-propylaniline (O-PA), through bond cleavage of the C-N bond, or together with CHPYD, it can hydrogenate to form decahydroquinoline (DHQ) . The rapid hydrogenation of Q to THQ causes the establishment of a pseudoequilibrium among this hydrogenated derivatives of quinoline [1]. As seen in the figure, this pathway indicates that removal of nitrogen from O-PA requires the hydrogenation of the aromatic ring, consuming more hydrogen in the reaction. Therefore, it is desirable to synthesize hydrodenitrogenation catalysts that will induce nitrogen removal from the molecule without full hydrogenation of the aromatic ring.

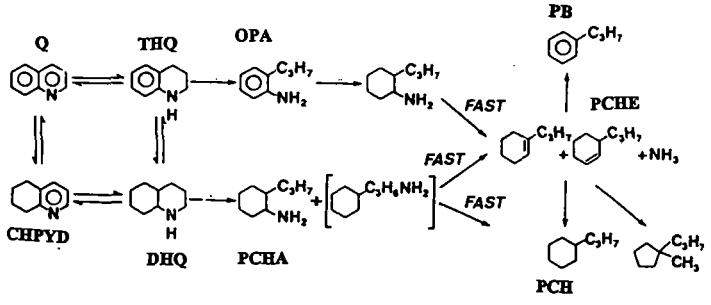

Figure 1
Reaction Pathway for quinoline HDN

It has been reported that nitrides and carbides of transition metals, specially Mo_2C and Mo_2N , synthesized by Temperature Programmed Reduction , posses high activity for heteroatom removal and hydrogenation of coal liquids and model compounds [5-7]. This work presents the results of the evaluation of the catalytic activity of Mo_2N, MoS_2 and Mo_2C ultrafine particle catalysts (UFP), synthesized by laser pyrolysis, for quinoline hydrodenitrogenation (HDN) .

EXPERIMENTAL

Mo-based ultrafine particle catalysts (Mo_2C, Mo_2N,MoS_2) were produced by laser pyrolysis from the reaction of $Mo(CO)_6$ with a gaseous reactant (NH_3, C_2H_4 or H_2S) followed by surface passivation in a flow of 5%O_2 balanced He at 300 K. The details of the experimental procedure and apparatus have been reported elsewhere [8,9].

The catalysts structure and morphology have been characterized by X-ray diffraction, high resolution-tranmission electron microscopy (HR-TEM) and thermogravimetry-mass spectrometry (TG-MS) [8-11]. The surface area was determined by the nitrogen BET method. The average composition of these particles was obtained by elemental analysis and the chemical state of the surface was characterized by X-ray photoelectron spectroscopy. Irreversible chemisorption of CO was used to measure the number of active sites on the catalyst surface.

Catalytic activity was evaluated using a stainless steel bomb microreactor, 22 cm^3 in volume, which was pressurized at 800 psi of hydrogen. A 5% catalyst loading with respect to a solution of quinoline dissolved in hexadecane was used. The reactor was maintained at 380°C for reaction periods of 15, 30 and 60 min while agitating at 440 rpm in a fluidized sand bath. The effect of the presence of added sulfur in the reaction was studied by adding dimethyl disulfide (DMDS) in 20% excess of the stoichiometric amount required to convert Mo_2N and Mo_2C to MoS_2. The liquid products were analyzed by gas chromatography with a fused-silica 30 m capillary DB5 column with a Flame Ionizing Detector. In this model compound reaction, the concentration of the liquid phase products is given as a mole percentage of quinoline initially charged to the reactor and normalized to 100%.

RESULTS AND DISCUSSION

Characterization

Table 1 summarizes the structural properties of these materials together with those from the commercial catalyst Shell 324.

TABLE 1

Catalyst	Surface area m^2/g	Crystallite size (nm)	Particle size (nm)	Site Density $x10^{15}cm^{-2}$
fcc Mo_2N	63	3	10	0.92
fcc Mo_2C	75	2	8.5	0.24
hex. MoS_2	86	2	4.3	na
Shell 324*	160	11	7.9	0.27

* From ref [12].

X-ray diffraction and HR-TEM have shown that Mo_2C and Mo_2N exhibit a face centered cubic structure whereas MoS_2 has an hexagonal structure. The crystallite size of the UFP catalysts was calculated from the full width at half maximum of the corresponding x-ray diffraction lines and the particle size from the value of the surface area of the particle using $Dp=6/\rho S$, where S is the surface area of the particle and ρ is the mass density. The difference observed between particle size and crystallite size indicates that these particles are partially agglomerated. Notice that Mo_2N posseses a density of active sites almost four times higher than that of Mo_2C. However the number of active sites measured is about half of the reported for materials synthesized by Temperature Programmed Reduction [6]. Elemental analysis gave an average composition for Mo_2N of $Mo_2N_{0.77}C_{0.5}$ and $Mo_2C_3O_{0.9}$ for the molybdenum carbide. Since this particles are so small, the high oxygen content observed in the results can be accounted for as an oxide monolayer of MoO_3 on the particle surface, as confirmed by XPS analysis [10].

Catalytic Activity

Figure 2 presents the results from the conversion of quinoline with respect to reaction time over Mo_2N, Mo_2C and MoS_2 UFP. It is observed that all three catalysts gave approximately the same high level of conversion. However, because there are numerous nitrogen-containing intermediate products, a high quinoline conversion does not necessarily correlate with high HDN conversion. In this case, quinoline was converted essentially into tetrahydroquinoline (THQ).

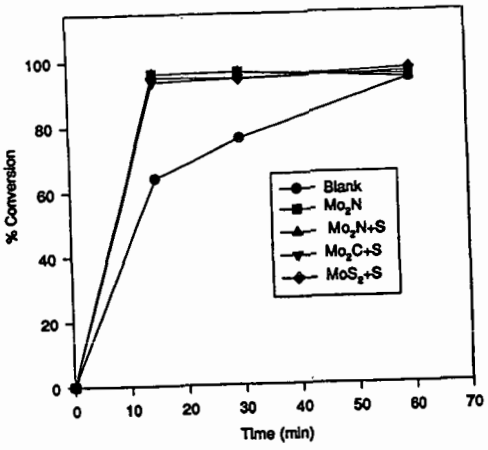

Figure 2
Conversion of quinoline with respect to time over Mo_2N, Mo_2C and MoS_2.

Figure 3 presents the product distribution for quinoline over the molybdenum nanoparticles after 30 minutes of reaction. The results are also compared to those of the commercial catalysts Shell 324 which was sulfided prior to the reaction.

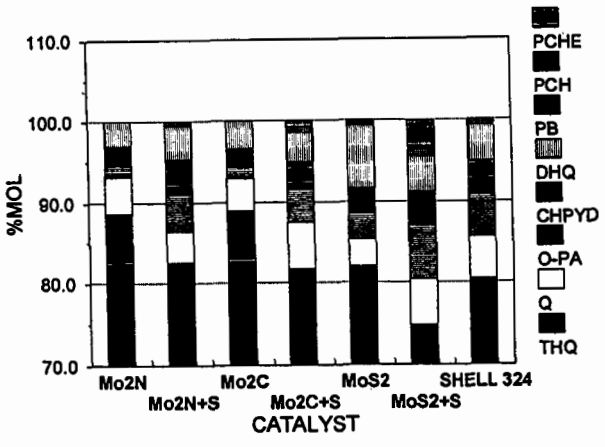

Figure 3. Product distribution after 30 minutes of reaction time

As it was previously mentioned, the main product of the reaction is THQ, in concentrations higher than 70% mol. This high concentration is thermodinamically favored by the elevated hydrogen pressure at which the reaction was carried out [1]. Mo_2C and Mo_2N gave very similar product distribution and concentration. This may be explained in terms of the similarity in surface composition observed from the xps analysis of these two catalysts [10]. Besides THQ, o-propylaniline (O-PA) , decahydroquinoline (DHQ) and cyclohexenopyridine (CHPYD) were also produced, while no denitrogenated products were detected. A higher concentration of DHQ (8%) and a small amount of propylbenzene (PB) were produced in the presence of MoS_2. Notice that Shell 324 gave similar conversion as MoS_2.

Longer reaction time periods (Figure 4) induced the conversion of tetrahydroquinoline (THQ) mainly into hydrogenated products, primarily decahydroquinoline (DHQ) with some THQ being dehydrogenated back to quinoline. Only small concentrations of nitrogen-free molecules were detected, less than a total of 1 % mol.

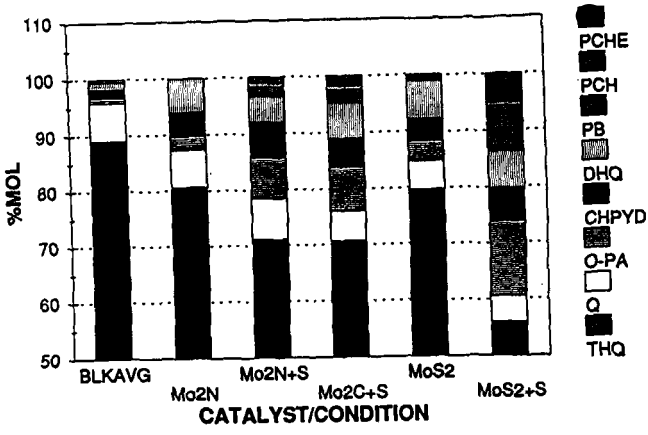

Figure 4. Product Distribution after 60 minutes of reaction time.

When excess sulfur was added to the reaction mixture, the concentration of THQ decreased, especially in the case of MoS_2, indicating that it was converted into other reaction products. Furthermore, the average concentration of hydrogenated products did not seem to be affected as much as the concentration of propylaniline (O-PA), which increased by more than 200% for the three catalysts. This fact agrees with previous reports that the presence of H_2S enhances hydrogenolysis reactions [1,2]. An increase in the concentration of denitrogenated compounds, mainly propylcyclohexane (PCH) and propylcylohexene (PCHE) was also observed. Only small concentrations of propylbenzene (PB) (~1-2%) were detected in the product mixture. This result agrees with the reaction pathway shown in figure 1. According to this figure, propylaniline (OPA) is hydrogenated to propylcyclohexylamine, which undergoes rapid denitrogenation to produce propylbenzene (PB), propylcyclohexene (PCHE) and propylbenzene (PB). In addition, decahydroquinoline (DHQ) undergoes hydrogenolysis of the C-N bond to produce propylcyclohexylamine.

Since the concentration of decahydroquinoline (DHQ) does not increase, but in some cases decreases, while the concentration of propylaniline (OPA) increases, it follows that the denitrogenation of decahydroquinoline (DHQ) is favored over the hydrogenation of O-PA. X-ray diffraction of the spent catalysts indicates that there is some transformation of Mo_2N and Mo_2C into MoS_2 after 60 minutes of reaction. This may explain why all three catalysts seem to follow the same reaction pathway.

HDN Activity

The Mo-based ultrafine particles exhibited low activity for HDN even in the presence of added sulfur. This low activity was unexpected, since there are reports of higher conversions and high selectivity for Mo2C and Mo2N catalysts, even under sulfur free conditions [6]. This outcome has been attributed in part to the presence of an oxide phase on the surface of these catalysts that may inhibit their activity [13,10].

Figure 5 presents % HDN as a function of time for the Mo-based UFP catalysts in the presence of added sulfur. As it was mentioned above, in the absence of sulfur very little denitrogenation was observed (less than 1%), even if the reaction was carried out for longer time periods or at higher temperatures (up to 2 hours, 400°C).

When H_2S was present, the denitrogenation of quinoline increased from 0.5% to 3 % for Mo_2N and to 4% for Mo_2C. Considering that Mo_2C has a lower number of active sites per unit area of catalyst, it follows that it is a more active catalyst than Mo_2N. As shown by figure 5,

MoS_2 was the most active catalyst since it gave the largest percent of denitrogenation (13%).

In terms of product selectivity, all three catalysts favored hydrogenated products over aromatic ones in the form of mixtures of propylcylohexane and propylcyclohexene.

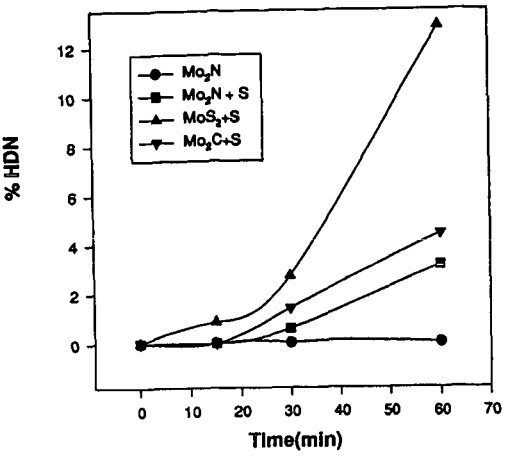

Figure 5
%HDN versus time for Mo_2N, Mo_2C and MoS_2 UFP catalysts.

CONCLUSIONS

Mo_2C, Mo_2N and MoS_2 ultrafine particle catalysts exhibited low activity and selectivity for the hydrodenitrogenation of quinoline. MoS_2 appears to be the most active catalysts . In the absence of sulfur, only less than 1% HDN was obtained with these catalysts. The addition of sulfur favored HDN activity by enhancing the hydrogenolysis of decahydroquinoline and tetrahydroquinoline. However, the improvement in activity was not very significant. The lower-than expected activity observed for this reaction, as well as for other model compound reactions tested [13], has been attributed to the presence of oxygen and amorphous carbon on the catalysts surface. In previous studies, it has been shown that surface composition has a large effect on the catalytic behavior of Mo_2C and Mo_2N specially for structure-sensitive reactions like hydrogenolysis and isomerization. Future studies to prevent or remove oxide coatings and to observe the effect on catalytic activity are underway

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